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CAN YOU TRUST YOUR PROCESS SIMULATION RESULTS

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Understanding both the limitations of process simulations and the assessments that can be performed to verify modeling results is important in the design and development of technical processes in many industries.

Chemical engineers routinely use process simulation software for design, troubleshooting, debottlenecking, and evaluating alternative processes. However, given the broad scope of results generated by simulators, and their ubiquitous use by practicing engineers, it is difficult to know when results may not be accurate [1] [2].

Although a simulation can be straightforward, it is not always easy to find errors that could affect the process study or design. Inaccurate simulation results in many cases can be traced back to the physical and thermodynamic properties package and associated calculation routines. In some cases, the user can correct the problem, for example choosing more suitable methods or entering more accurate model parameters. In other cases, the operating conditions may be outside the intended range of the model or there may be an error within the program itself. Sometimes, a specific property package can generate inaccurate properties due to:

- internal thermodynamic inconsistencies,
- inappropriate modelling choices set by the property package,
- poor data fitting,
- or more commonly lack of underlying experimental data for mixtures.

This article presents collective experiences of process chemical engineers at the authoring companies to describe the lessons learned when careful inspection of simulations revealed errors.

The examples draw from projects in many different industries, using several different process simulation packages and physical property estimation programs.

PHYSICAL PROPERTIES

Process simulators use predicted physical properties to calculate process design parameters such as heat exchanger duties, pump and compressor power requirements, line sizes, and distillation column sizes. Examples of how simulators have had trouble correctly predicting physical properties are presented below. In the examples, simulation results had to be checked against known values to identify the problem. If an inaccurate result is found, the user must adjust the methods used by simulator or use external calculations to get the required information for the process being studied.

Heat capacity. One example involves the development of a process simulation for a beverage grade CO_2 plant with a water scrubber to remove polar impurities such as ethanol. The water is chilled before it is fed to the scrubber, as shown in Figure 1. Typically, an activity coefficient model is selected for simulating the water scrubber equipment. In the simulation, the model accurately estimated removal of the polar impurities, but unexpectedly reported an inaccurate heat capacity for water that was 10% lower than the true value. The incorrect heat capacity could have resulted in under sizing the water cooler and underestimating the amount of cooling medium required.

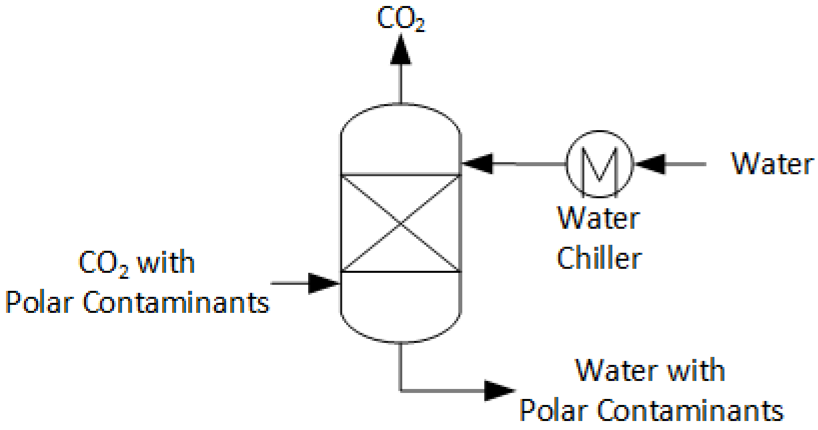


Figure 1 -A Simple Water Scrubber Becomes a Challenge to Simulate.

The activity coefficient model chosen could accurately predict solubilities in the water scrubber but could not accurately predict the heat capacity of pure water in the water chiller. It was determined that the activity coefficient model was coupled with a heat capacity model that was wrong for the application. Choosing a different property package fixed the heat capacity for water but simultaneously caused the thermal conductivity to be severely overestimated. Ultimately, the best simulation approach was to change only the liquid thermal property calculation method. Changing a property package can result in unexpected changes to subordinate property methods and results, so all outputs must be carefully checked after such a change.

In another example, an error was discovered in the heat capacity prediction for propylene glycol for a utility cooling system. Surprisingly, the simulated heat capacity was about *half* the value shown in multiple sources in literature. A similar problem was also encountered with the heat capacity of liquid propane in a refrigeration system. The heat capacity for liquid propane was in error by about 10% compared to the known values for propane reported in standard tables [3] of properties of refrigerants. In both cases, no workaround was found in the simulation, and the results were manually corrected to properly specify the process equipment.

Density. Density is critical for engineering calculations such as pump sizing and line sizing. The choice of an equation of state or how it is used within a property package can cause inaccurate density results, even if phase equilibrium results are accurate. Liquid density calculation methods are typically accurate only for specific types of liquids. For example, a property package that accurately predicts liquid hydrocarbon densities may be significantly inaccurate for pure water at room temperature. Densities should be cross-checked with known physical property data for the specific conditions being modeled. Inaccuracies can often be addressed by choosing a different property package.

Viscosity. Viscosity is important for pump sizing, column sizing, pressure drop estimates, and determination of heat transfer coefficients for heat exchanger sizing. A glycerol and water mixture is an example of a system for which it is particularly difficult to accurately predict viscosity over the range of temperatures present throughout a process. The dynamic viscosity of a 95 wt% glycerol mixture with water changes over 50-fold when it is cooled from 212°F to room temperature. For comparison, the viscosity of water changes less than 5-fold over the same temperature range. The authors have had “mixed” results with simulators accurately predicting the viscosity of such a glycerol / water mixture. Default parameters within simulation databases may not be accurate across the entire process range or may not exist at all. In some cases, the user may need to regress viscosity data to generate property parameters for the simulation.

Fluids near the critical point. Special attention is required for fluids near their critical point, particularly for supercritical mixtures. Supercritical CO_2 or light hydrocarbons are commonly encountered in the oil and gas industry. Supercritical fluids are also common in silicon processing. In the supercritical region, especially near the critical point, small changes in temperature or pressure can result in extreme changes in heat capacity and density, potentially resulting in process design errors if simulation results are trusted without careful review.

The critical point of CO_2 is 88°F (31°C) and 1071 psia (7383 kPa). Consider the heat capacity of CO_2 near the critical point at 1200 psia as shown in Figure 2. The pronounced peak in heat capacity has implications for heat exchanger designs, which are sometimes based on the Log Mean Temperature Difference (LMTD) method. LMTD is a simple way to account for non-constant driving force between the cold and hot fluids inside a heat exchanger. The mathematical derivation of LMTD requires an assumption of constant heat capacity. However, as shown in Figure 2, the heat capacity for supercritical CO_2 is not constant.

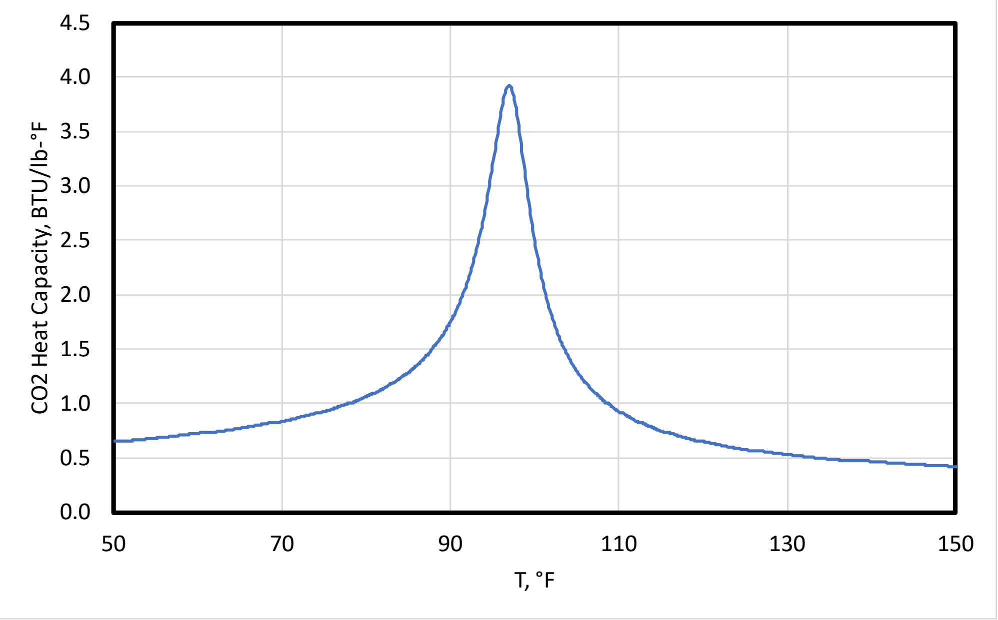


Figure 2 - Heat Capacity of CO_2 Near the Critical Point at 1200 psia.

An example heat exchanger duty curve for an after-cooler of a supercritical CO_2 compressor is shown in Figure 3. The inflections in the CO_2 curve result in less driving force than would be predicted if the LMTD formula was used naively, which would result in an undersized exchanger with < 90% of the truly required heat transfer area. For this application, the actual Mean Temperature Difference (MTD) must be used (the MTD is defined by $Q = UA*[MTD]$).

This example demonstrates the importance of closely scrutinizing predicted physical properties to make sure the true behavior of the system is reflected. Moreover, how those properties are used in equipment calculations should be investigated to ensure the methods are rigorous enough for the system being simulated.

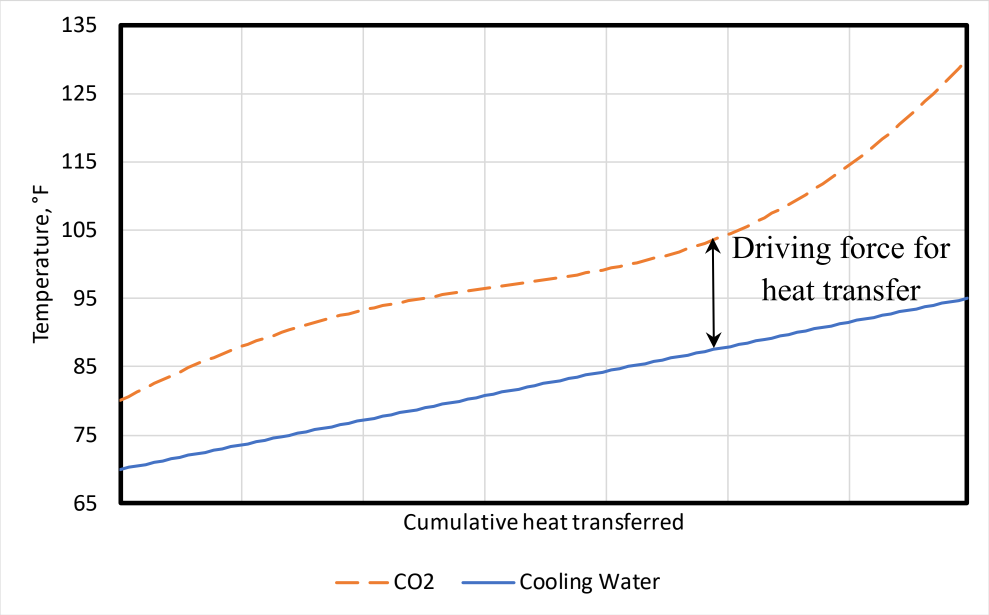


Figure 3 - Duty Curve for Supercritical CO_2 Compressor Aftercooler at 1200 psia.

A further complication with simulating supercritical fluids is that they are sometimes classified arbitrarily as either a vapor or a liquid by the simulator, which can lead to computational problems when working near the phase boundary. The density and compressibility of a stream near the critical point should be checked to determine if it is expected to behave more like a liquid or vapor. This is important when selecting equipment for increasing the pressure of a supercritical fluid. A compressor may be needed at lower pressures, but once the fluid is sufficiently dense a pump could potentially be used to further increase the pressure of the stream.

The expected phase of the fluid may also affect the selection of the property package. For example, one property package may be most accurate for lower pressure CO_2 capture-related simulations when the CO_2 is in the vapor state. A different property package may be more appropriate for simulating CO_2 compression or dense-phase pumping once the supercritical pressure is reached. The applicability of a property package should be evaluated at several locations in a flowsheet to determine if it accurately characterizes the thermodynamic and physical properties of the entire system.

VAPOR-LIQUID EQUILIBRIA

Simulators use vapor-liquid equilibria (VLE) for many calculations, such as separation of components in distillation columns using both equilibrium or rate-based calculations, calculating absorption or stripping efficiencies for packed columns, estimating solvent losses from an absorber, and estimating vapor losses in a separator or flash vessel. Choosing an appropriate VLE model along with validation checks is a crucial part of accurately predicting system performance. Since VLE models are built on assumptions of how components interact, selecting the wrong model will produce poor predictions of the system behavior, no matter the quality of the simulation setup and input. Below is a summary of VLE parameters to verify in process simulations, along with examples of problems that might be encountered.

Vapor pressure. Simulation-generated properties should be checked at all relevant operating conditions that may occur within the process. For example, the vapor pressure of a solvent could be accurate at the lower temperature conditions in an absorber while being inaccurate at the higher temperature conditions of the desorber. An error like this could result in an incorrectly sized overhead condenser.

A common source of inaccuracy for vapor pressure comes from approximations made by the user when modelling hydrocarbon streams. When creating hydrocarbon streams in process simulators, the composition of the light ends can dramatically affect the vapor pressure of the mixture. However, laboratory analysis of hydrocarbon samples may not include speciation of light ends such as methane, ethane, or propane. The components may be present in the stream in small amounts but are simply not included in the analysis due to sampling or analysis methods. Sometimes light ends are lumped into a group such as $C_1 – C_3$ components. This can cause the predicted vapor pressure from a simulation to be much lower than reality. For example, consider an oil stream encountered that was 95 wt% $C_6 – C_{10}$ hydrocarbons with less than one weight percent total of methane, ethane, and propane. The balance was C_{10+} hydrocarbons. At 100°F, this stream was estimated to have a vapor pressure of 9.3 psia. If the $C_1 – C_3$ components were not accounted for, the estimated vapor pressure was only 3.8 psia, representing a difference of 5.5 psi. This problem could cause estimates for volatile organic compound (VOC) emissions to be much lower than reality. Missing lighter components also affects the predicted bubble point temperature. Similarly, neglecting or lumping together the heaviest components will affect the predicted dew point temperature. Lumping of distributions of components as pseudo components, hypotheticals, or surrogates are likely to cause this kind of error.

Binary interaction parameters for liquid activity coefficient models. Non-ideal liquid mixtures are frequently modeled using liquid activity coefficient models to determine the phase behavior of a mixture. Often, activity coefficients are estimated using binary interaction parameters derived from experimental data for binary mixtures. Phase equilibria for multicomponent mixtures can be reliably estimated using accurate correlations and mixing rules. However, there are many places where simulation results could go amiss when estimating phase equilibria.

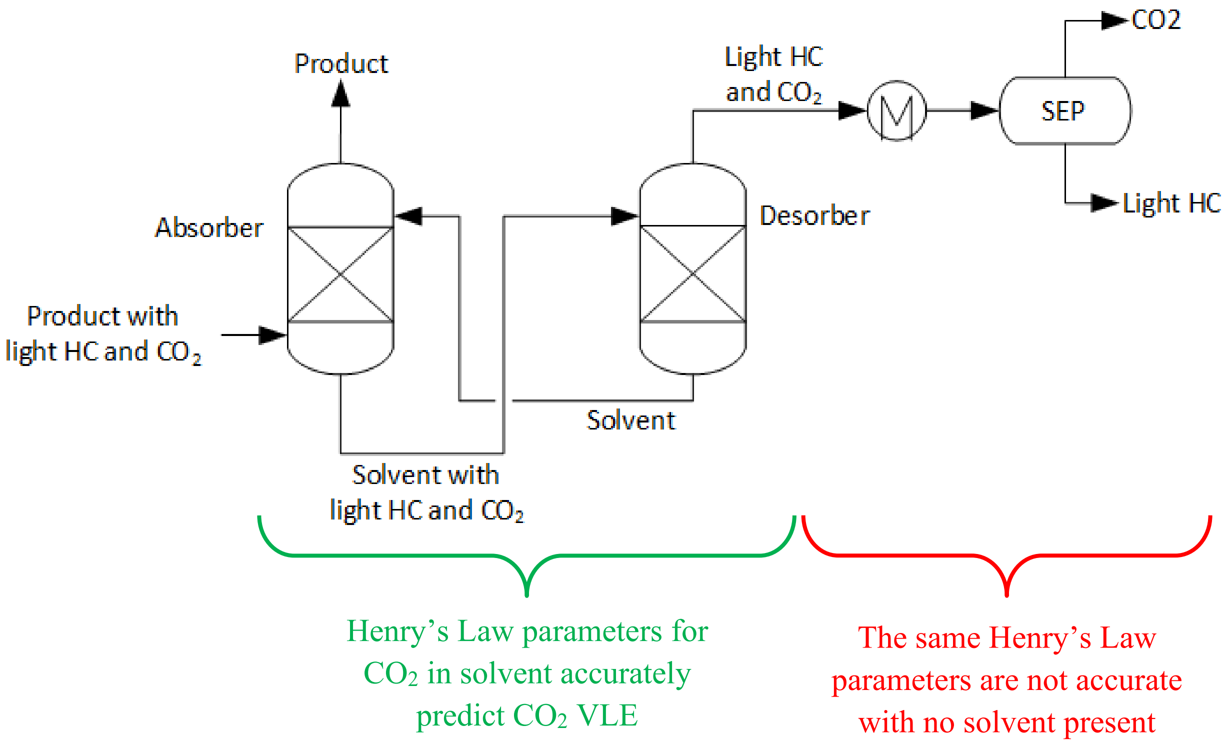
First, a simulation property package may not have experimentally based binary interaction parameters available for the component pairs of interest. In this case, simulators may default to estimating activity coefficients with semi-empirical group contribution methods such as UNIFAC. Alternately, if interaction data are available for some components in a mixture and not others, the simulator may completely ignore any interaction between the pairs for which data are missing, or assume the interactions are the same as between similar components.

Problems can also arise if the user relies on simulation results when the approach used is wrong for the situation. Generally, it is not evident which approach the simulator is using unless the user specifically investigates the issue. As a further complication, it is often not evident which approach is required to get the expected accuracy. Sometimes it may be adequate to use UNIFAC to estimate activity coefficients or to assume ideal interactions for certain pairs. In other cases, these approaches could lead to errors that have a detrimental effect on the equipment design.

When VLE predictions are important, users should investigate the method the simulator is using for all pertinent pairs of components. Oversights are more likely to occur when there are many components in the simulation, when the most important interactions change throughout the flowsheet, or when there are trace components that are not of primary concern but can still significantly impact the equipment design.

The authors worked on a process simulation for a water scrubber designed to remove polar compounds such as methanol and ethanol from a gas stream consisting primarily of CO_2. The CO_2 stream also contained trace amounts of hexane, and the simulation predicted that the scrubber would remove all the hexane from the gas. Closer examination of the binary interaction parameters revealed that there were no NRTL parameters in the simulation for hexane and water. The simulation reverted to ideal solution behavior because of the missing interaction parameters and overestimated the removal of hexane in the water scrubber. If left unnoticed, the downstream hydrocarbon removal beds might have been sized for an inappropriately low hydrocarbon load.

Another challenging situation is when the pertinent pairs change throughout the flowsheet. This was observed when a process simulation was developed that included recovery of a light hydrocarbon product through absorption into a solvent, desorption of the light hydrocarbon, and separation of the product from CO_2 and other light impurities, as shown in Figure 4. CO_2 was selected as a Henry's Law component in the simulation and Henry's Law parameters were manually entered for CO_2 in the solvent. Initially, binary parameters for CO_2 and the light hydrocarbon product were not included.



Henry's Law parameters for CO_2 in solvent accurately predict CO_2 VLE

The same Henry's Law parameters are not accurate with no solvent present

Figure 4 - Different VLE Models Needed in Different Parts of Flowsheet.

The simulator accurately predicted the phase behavior of CO_2 in the absorption and desorption sections based on the user-supplied Henry's Law parameters. However, the simulator did not behave as expected in a downstream separator vessel where the primary components were the light hydrocarbon and CO_2. Only trace amounts of solvent were present in this separator. The simulator calculated the VLE of CO_2 in the mixture based solely on the interaction of CO_2 with the ppm levels of solvent in the liquid. The simulator ignored the interaction of CO_2 with the light hydrocarbon, which composed 95% of the liquid phase in the separator, because there were no Henry's Law parameters for that pair.

In this case, the most accurate way to model VLE for CO_2 was different between different sections of the simulation. Further investigation revealed that the simulator was behaving exactly as the user manual indicated – it was ignoring pairs for which no binary interaction parameters were supplied or available. However, this could potentially be overlooked if the simulation contains many pertinent pairs, and the user is unsuspecting of the default calculation method. If left unnoticed, this error could result in the design of a separation process that cannot meet product specifications. Complex activity coefficient models that make use of interaction parameters require scrutiny of results before they can be trusted with certainty.

Solubilities of inert components. The solubilities of inert components in simulations are often overlooked. In many cases, they are not important because they are non-reactive and tend to be present in liquids at ppm levels. However, inert solubilities can be important when considering non-condensable gases that can accumulate in recycle streams or when calculating vapor pressure to estimate the net positive suction head available (NPSHA) [4] for a pump. Sometimes issues arise because the simulation does not accurately predict the solubility of the inert components; other times, through oversight, the user neglects to include inert components in the simulation.

One example involves a situation at a plant that was experiencing poor condenser performance on a distillation column. A potential cause of the problem was that the feed stream was sometimes lighter in composition than was predicted by the process simulation. It was discovered that the feed was coming from a tank (operating at a higher pressure than the distillation column) with a nitrogen blanket. The plant had not considered nitrogen as a component in the feed stream for the simulation, but it turned out that a significant amount of nitrogen was soluble in the feed at the storage tank operating conditions. In this case, nitrogen was degassing in the lower pressure distillation column, getting trapped in the total condenser, and adversely affecting condenser performance. Conversely, if nitrogen were soluble at the condenser operating conditions, the vapor pressure of the liquid from the condenser would be significantly higher than predicted by the simulation. Ignoring the inert gases would cause an error in the NPSHA calculations for the condensate pump and could lead to pump cavitation. For this example, both recognizing the presence of inert components and accurately accounting for the solubility of non-condensables were critical to understanding the operation of the condenser system.

HEAT EXCHANGER DESIGN

Multiple methods can be used to estimate heat exchanger duties, and it is not always clear what method is used by the simulator. When there is no phase change in the heat exchanger, the duty can be calculated with Equation (1).

$$Q = m \int_{T1}^{T2} c_p dT \tag{1}$$

Where:

Q = duty in BTU/hr

m = mass flow rate in lb/hr

c_P = specific heat capacity in BTU/lb -°F, usually a function of temperature

T1 = initial stream temperature, °F

T2 = final stream temperature, °F

Another way to calculate heat exchanger duties is by Equation (2). This method is accurate whether or not phase change occurs in the exchanger.

$$Q = m(H_{out}-H_{in}) \tag{2}$$

Where:

H = stream enthalpy in BTU/lb

Finally, for many simple heat exchanger applications, the heat exchanger duties can be calculated from the area and log mean temperature difference (LMTD) of the exchanger using Equation (3).

$$Q = U*A*LMTD \tag{3}$$

Where:

$$\text{LMTD} = \frac{\Delta T_A - \Delta T_B}{\ln \Delta T_A - \ln \Delta T_B} \tag{4}$$

ΔT_A = the temperature difference between the hot stream inlet and cold stream outlet in °F

ΔT_B = the temperature difference between the hot stream outlet and cold stream inlet in °F

When relying on process simulation tools for heat exchanger performance, the heat exchanger duty should be calculated independently of the simulation. Some simulators calculate the exchanger duty from the stream enthalpy rather than the heat capacity and temperature difference. In some instances, there are problems with the estimates for stream enthalpy, which results in a discrepancy in the duty calculated by the different methods. This means that even though the user has verified the heat capacities of the streams in and out of the exchanger are accurate, the exchanger duty reported by the simulation could still be inaccurate and thermodynamic inconsistencies may be present in the model.

Heat exchangers should also be checked for a temperature cross, particularly if a phase change occurs. Some process simulators give errors or warnings when a temperature cross is predicted, but some simulators do not and may only check the inlets and outlets to verify the energy balance. When a heat exchanger is modelled as two single-stream exchanger blocks connected by an energy stream then checking for temperature crosses becomes even more important. For example, the authors were asked to perform a feasibility study and check the work for a particular heat exchanger design. During review of the simulation, a temperature cross was discovered in the middle of the heat exchanger. By simply observing the inlet and outlet temperatures of the heat exchanger, the behavior appeared not to have a temperature cross.

However, in this example, there was a phase change for one of the fluids in the heat exchanger. Figure 5 shows the temperature for both fluids in the heat exchanger as a function of the duty.

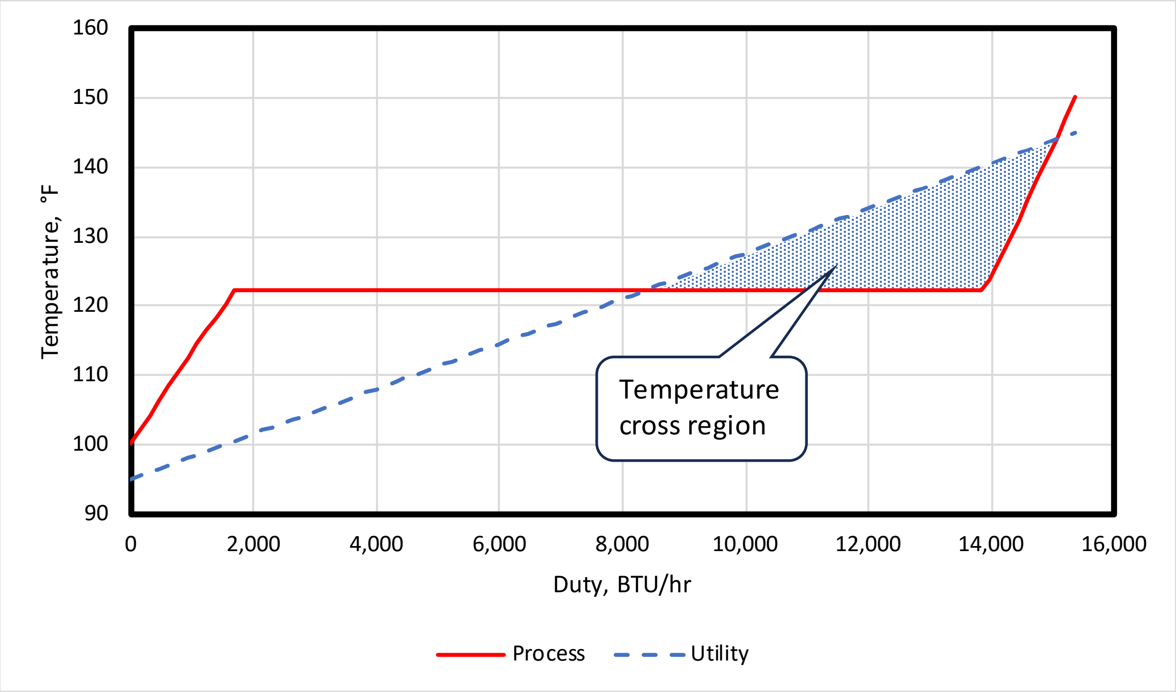


Figure 5 - Example Temperature Cross During Phase Change.

Understanding how the simulator reports the LMTD or MTD (mean temperature difference) in the case of a heat exchanger with a phase change can be important as well. For some heat exchangers, the MTD is approximately equal to LMTD, but in others it is not. LMTD assumes a constant heat capacity and is not valid when a phase change occurs, such as a vapor that is desuperheated, condensed, and then subcooled as in the example above. Inconsistent reporting conventions between different simulators can add to the challenge of understanding simulation results. Some simulators report the true MTD, while others report the true MTD but label it LMTD, and still others will report the LMTD even when it is invalid because phase change occurs. It is important to carefully consider how the LMTD is being applied to avoid problems with heat exchangers that are significantly under-sized.

WATER CONTENT OF STREAMS

The water content of a stream is especially important when a gaseous stream saturated with water is fed to a dryer or dehydration system since the design of this equipment largely depends on the amount of water being removed. The water predicted by a simulator should be checked against literature sources, software explicitly designed for estimating water content, and other simulation tools or property packages.

In one specific example, desiccant dryers at a CO_2 plant were becoming saturated with water earlier than expected during the adsorption cycle, and wet gas was exiting the dryers. It seemed that the dryers were undersized. It was determined that the design material balance was based on a simulator's default equation of state (EOS). This default EOS underestimated the water content of the CO_2 stream by about 20%. In this case, the under design of the driers could have been avoided if the engineer had double-checked the water content against readily available literature values.

REACTIVE SPECIES AND ELECTROLYTES

Systems with reactive species and electrolytes are notoriously difficult to model accurately. Care must be taken in selecting the proper simulator and property package, and in verifying and/or specifying the reaction chemistry. The heat of reaction should be confirmed, particularly if a significant temperature change is expected. Thermodynamic consistency of equilibrium constants and derived properties like heat capacity should be independently checked. The authors were once asked to troubleshoot an undersized carbonyl sulfide (COS) hydrolysis reactor. Different simulators were not in agreement on the COS equilibrium constant, which defines the extent of the reaction at equilibrium. The discrepancy was traced back to erroneous enthalpy of formation data for the reactants in some of the default physical property packages.

The solubility of ionizable and reactive species may be underpredicted if the chemistry is not adequately represented in the simulation. An example of this is aqueous scrubbing of a vapor to remove NH_3 and CO_2. Under typical process conditions, NH_3 and CO_2 will react in the liquid water phase to produce ammonium carbonate or ammonium bicarbonate. If this reaction is not accounted for, the simulator will underpredict the amount of NH_3 and CO_2 that are absorbed into the liquid. Other reactive species that are difficult to simulate include formaldehyde and sulfur vapors. Formaldehyde can form dimers and trimers and react with methanol. Sulfur vapors distribute between species such as S_2, S_4, S_6, and S_8, leading to changes in volume and heat capacity of sulfur vapor streams at different temperatures.

Neglecting the effects of contaminant acids or bases or salts, even those at very low concentrations, can lead to inaccurate simulations. This is especially the case where changes in pH control the dynamics of a system. An example of this is H_2S removal using aqueous amine solvents. In some standard designs, acid components are used as stripping promoters which function by shifting chemical equilibrium in the desorber allowing for lower lean loadings. Heat stable salt contaminants (acid-base pairs) can disrupt the chemistry to the point of causing significant changes to solvent behavior [5], leading to either improved or degraded acid gas capture. Neglecting or improper lumping of degradation products may have similar influences on systems relying on pH buffer. Thorough and accurate analysis of compositions is a crucial input into a reactive/electrolyte simulation.

CONCLUSION

Simulators are highly useful tools that make a chemical engineer's job more efficient. However, no simulator or user is perfect. Default settings, bugs in the software, and user errors can be detrimental to process design if left unchecked. Chemical engineers should not take simulation results at face value, but rather do sanity checks of the simulation and confirm critical data against literature sources. This is especially important for results that have a strong influence on real world decisions. Trust the simulation but verify the results.

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